

AD-A242 833



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GRANT N00014-89-J-1178

R&T Code 413Q001-05

TECHNICAL REPORT NO. #35

An In-Situ Spectroscopic Ellipsometry Study Of The Electron  
Cyclotron Resonance Plasma Oxidation Of Silicon And Interfacial

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Submitted to the  
Journal of Applied Physical Letters

91-16641



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91 11 27 044

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>unclassified</b>		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #35		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION UNC Chemistry Department	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research (Code 413)	
6c. ADDRESS (City, State and ZIP Code) CB# 13290, Venable Hall University of North Carolina Chapel Hill, NC 27599-3290		7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Grant #N00014-89-J-1178	
8c. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street, Arlington, VA 22217		10. SOURCE OF FUNDING NOS.	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT NO.
11. TITLE (Include Security Classification) <b>AN IN-SITU SPECTROSCOPIC ELLIPSOMETRY STUDY OF THE ELECTRON CYCLOTRON RESONANCE PLASMA OXIDATION OF SILICON AND INTERFACIAL</b>			
12. PERSONAL AUTHOR(S) Y.Z. Hu, J. Joseph* and E. A. Irene			
13a. TYPE OF REPORT Interim Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Yr., Mo., Day) November 1991	15. PAGE COUNT 13
16. SUPPLEMENTARY NOTATION Journal of Applied Physical Letters			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB. GR.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The growth of SiO <sub>2</sub> films on Si and the evolution of interfacial damage resulting from electron cyclotron resonance plasma oxidation was studied using in-situ during process spectroscopic ellipsometry. Accelerated growth under positive substrate bias indicates that negative atomic dominate the growth above an oxide thickness of 4 nm. Below this thickness bias appears less important. The interfacial damage is different in both nature and extent from that caused by ions with higher energies. It appears that the damage layer is composed of SiO <sub>2</sub> with a-Si and is due to the oxidation reaction rather than the ions from the plasma.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Mark Ross	22b. TELEPHONE NUMBER (Include Area Code) (202) 696 - 4410	22c. OFFICE SYMBOL	

An In-Situ Spectroscopic Ellipsometry Study of the Electron  
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Accession For	
N. 000001	
DTIC Tab	
Document used	
Justification	
By	
Distribution/	
Availability code	
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A-1	

Abstract

The growth of SiO<sub>2</sub> films on Si and the evolution of interfacial damage resulting from electron cyclotron resonance plasma oxidation was studied using in-situ during process spectroscopic ellipsometry. Accelerated growth under positive substrate bias indicates that negative atomic species dominate the growth above an oxide thickness of 4 nm. Below this thickness bias appears less important. The interfacial damage is different in both nature and extent from that caused by ions with higher energies. It appears that the damage layer is composed of SiO<sub>2</sub> with a-Si and is due to the oxidation reaction rather than the ions from the plasma.

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The use of plasmas to grow  $\text{SiO}_2$  films on Si for electronic applications dates to the beginning of the Si technology<sup>1</sup>. However successful these early workers were at producing oxide films, the electronic quality of the films and particularly the Si-SiO<sub>2</sub> interface was not adequate for device applications. More recent attempts<sup>2,4</sup> were far more successful at attacking the interfacial quality issue, but the best processes usually included elevated temperatures in oxygen either before or during plasma treatment or both. Recent research on plasma processing shifted to producing chemically vapor deposited, CVD, oxides of nearly the same quality as produced by thermal oxidation with the use of both local and remote plasma techniques configured to reduce interface damage<sup>5,7</sup>. Considerable research underlies the belief that the energetic plasma and/or ion beam processes produce substrate damage concurrently with film formation<sup>2,3</sup>. We (and many others) have used in-situ during process, ISDP, spectroscopic ellipsometry, SE, to study the production of damage along with surface cleaning, film etching and film growth.

The present study uses ISDP SE in the electron cyclotron resonance, ECR, oxygen plasma environment to investigate the early stages of plasma oxidation of Si. We report conditions which enhance the plasma growth, minimize Si damage and yield information relative to the plasma oxidation mechanism. X-ray photoelectron spectroscopy, XPS, was also performed to confirm the SE results. We report that the damage measured by SE analysis is located on the oxide side of the Si-SiO<sub>2</sub> interface and due to the oxidation

reaction at the Si-SiO<sub>2</sub> interface. This damage is decidedly different in nature than the crystallographic damage seen with ion beam processing.

Plasma oxidation was performed on high resistivity Si wafers that were cleaned<sup>9</sup> and placed in a vacuum chamber equipped with a homemade ECR plasma source and high precision automated spectroscopic ellipsometer. The system with SE characteristics and alignment procedures were previously described<sup>10,11</sup> and applied to ion beam studies. The plasma conditions were: 300W, oxygen pressure of  $5 \times 10^{-4}$  torr which resulted in a sample temperature during oxidation of about 80°C. The results that follow were made with the sample normal to the plasma and with sample biases of 0V, +30V and -30V. The bias conditions were chosen to be above the +17V plasma potential. The sample would be negative with respect to the plasma at both 0V and -30V, and positive only at +30V applied sample bias.

Fig. 1a shows a typical pseudo-dielectric function,  $\langle \epsilon \rangle$ , set of spectra as obtained from SE, in terms of both  $\epsilon_1$  and  $\epsilon_2$  versus photon energy, as a function of oxygen plasma exposure time, the oxidation time, for normal incidence of the plasma source with the sample surface, and with an applied substrate bias of 0V. Fig. 1a is representative in that no new spectral features were observed under the other experimental conditions, and the data are analyzed (below) using a best fit optical model in terms of oxide and damage layer thicknesses. In order to analyze the measured  $\langle \epsilon \rangle$  data, we use the Bruggeman effective medium approximation, BEMA, with two discrete but compositionally inhomogeneous films. We do not

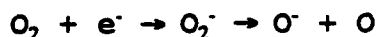
exhaustively justify this approach here, but there exists considerable work both in our laboratory<sup>10-12</sup> and elsewhere<sup>13-16</sup> where this model has been found to yield excellent results that are concordant with both the SE results and independent measurements of the SE obtained parameters. In this model film 1 is the top layer which in our case is the plasma grown oxide, and film 2 is the damaged layer in between the pure  $\text{SiO}_2$  and the c-Si substrate. Film 2 has been found from the present BEMA analysis to be composed of  $\text{SiO}_2$  and a-Si. In the course of the present research we have assumed that film 1 can also be damaged and we used fractions of a-Si to represent the damage; we have also assumed that a damaged layer exists both above and below film 1; and we have tried models where one or both of the above mentioned components of film 2 are absent as well as also containing fractions of c-Si and voids. The results show that the best fits were consistently obtained using the model shown in the inset of Fig. 1b which indicates a pure  $\text{SiO}_2$  film, film 1, on a damaged layer, inhomogeneous layer, film 2, composed of  $\text{SiO}_2$  plus a-Si, on a c-Si surface. This model is in accord with all of our results and will therefore be used throughout this study. Fig. 1b also shows a typical fit of the data to the model with the parameters  $L_1$ ,  $L_2$ , and volume fractions of constituents for film 2, and  $\delta$ , the unbiased estimator which relates the quality of the fit. This model is considerably different from that found for the case of ion beam damage where film 2 was composed of c-Si, a-Si and voids. This suggests a different damage level and extent associated with ECR plasma

processing. The BEMA fits also enable the extraction of  $\text{SiO}_2$  film thicknesses which were independently checked by angle resolved x-ray photoelectron spectroscopy, from which the Si 2p spectra showed the presence of an  $\text{SiO}_2$  film with a peak near 103.5 eV and the unoxidized Si peak near 99 eV.  $\text{SiO}_2$  film thickness values obtained from the appearance of the Si substrate peak at various angles were compared with the SE BEMA value on the same sample. In one typical case XPS gave an average thickness of  $6.7 \pm 0.5$  nm and ellipsometry yielded a value of 7.2 nm.

Figure 2 shows the BEMA analyzed thickness values for film 1, the plasma oxide, and film 2 the interface damage layer as a function of oxidation time, for three substrate biases. We first focus on the longer oxidation times where a self limiting oxidation is seen without a sample bias. That the oxidation becomes self limiting implies that about a 3nm oxide provides a barrier to further oxidation which slows to produce less than 5 nm in two hours. With the addition of sample bias the situation is altered considerably. Specifically, the positive sample bias enhances the oxidation rate by five fold beyond a film thickness of 3 nm producing oxide at about 2.5nm/hr as compared to .5nm/hr for zero bias in the same thickness regime. Alternatively, the negative bias significantly reduces the rate, if not completely stops growth, in the same time interval. We therefore conclude that negative oxygen related plasma species are primarily responsible for the oxide growth in the transport limited regime beyond 3 nm, and this is in accord with previous marker studies of plasma

oxidation<sup>17</sup>.

In the very initial regime of growth below 3nm, the effect of bias is less clear. In Fig. 2 it is seen that in the initial regime all the applied sample bias conditions yield about the same oxidation rate. For an explanation consistent with the results, we first consider that the high density of electrons in the plasma promote electron attachment to  $O_2$  via a favored interaction to produce a molecular ion,  $O_2^-$ , that is less stable than  $O_2$  and more readily decomposes to atomic species<sup>18</sup> according to the following:



The  $O^-$  can readily migrate through the oxide with positive sample bias. For negative sample bias, however, the molecular ion  $O_2^+$  predominates at the outer oxide surface, and this larger species (compared to  $O^-$ ) is less likely to migrate rapidly through an oxide at low temperatures, or to decompose to atomic species. Prior to oxide barrier formation, when the oxide is too thin to present a diffusion barrier, the oxidant species react readily and similarly with the Si surface and bias presents only second order effects. In this case both bias polarities simply attract ionic species in addition to neutrals, thereby slightly increasing the oxidation rate over the unbiased case in the earliest oxidation regime.

As was mentioned above the damage layer observed as a result of ECR plasma oxidation shows no crystallographic damage in the Si surface, but rather an inhomogeneous oxide interlayer in between the c-Si substrate and stoichiometric  $SiO_2$ . It is seen in Fig. 2 that for all bias conditions at least 3/4 of the damage layer forms



early (within seconds) in the oxidation process, and afterwards changes little with further oxidation. The fact that the damage layer reaches a steady state thickness is not easily rationalized. As the oxide film thickens, the Si surface should become further screened from exposure to damaging moieties from the plasma, and at the same time the damage at the Si surface is being consumed via the oxidation reaction. Thus, the consumption and screening of the Si surface suggests that a decrease in the damage layer is to be anticipated as oxidation proceeds.

The fact that a decrease in the damage layer is not observed during oxidation strongly suggests that the oxidation reaction itself, with the attendant large change in molar volume at the Si-SiO<sub>2</sub> interface during the conversion of Si to SiO<sub>2</sub><sup>19</sup> can contribute to the damage layer in the form of a-Si, as is required by the BEMA in order to obtain the best fit. Considerable evidence exists (see for example the reviews refs 20 and 21 with references therein) which give evidence for a chemically and structurally disordered interfacial region as a result of oxidation alone. Furthermore, and more specifically, SE studies using BEMA analysis confirm that the Si-SiO<sub>2</sub> interface is best modeled using an interfacial layer that is composed of a volume fraction of a-Si<sup>22</sup>. This would be especially true for all temperatures below the Si crystallization temperature of about 500°C. It appears that oxidation significantly contributes to the damage layer when the ion or other damage mechanisms contribute little, namely when the total damage is small as with the ECR plasma.

The authors are grateful for support of this research by NSF through an Engineering Research Center at NC State Univ, and by the Office of Naval Research, ONR.

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## List of Figures

Figure 1 (a) Typical spectroscopic ellipsometry pseudo-dielectric function spectra as a function of exposure time to the ECR Plasma. (b) Typical Bruggeman effective medium approximation, BEMA, fit of the data (open circles) to the BEMA for the model (solid line) using the optical model in the inset. The fit yields values for  $L_1$  and  $L_2$  and volume fractions of components and  $\delta$ , the unbiased estimator, which measures the quality of the fit.

Figure 2 ECR plasma oxidation results from the BEMA fits to the in-situ SE data yielding the oxide thickness (solid lines) and damage layer thickness (dashed lines) for various applied biases and at  $0^\circ$  incidence.

